

METHANE: A BUNCH OF INFORMATION FOR CLIMATE RESEARCH

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Abstract: Methane is a radiatively and chemically active trace gas of the earth's atmosphere. Its atmospheric concentration has been measured continuously and directly since 1978 (STEELE *et al.*, J. Atmos. Chem., 5, 125, 1987; BLAKE and ROWLAND, Science, 239, 1129, 1988; DLUGOKENCKY *et al.*, J. Geophys. Res., 99, 17021, 1994). Before that the CH₄ concentration history has to be reconstructed from paleo records. Ice sheets and glaciers are so far the only archives which have stored the atmospheric gas composition directly. Results from various ice cores are consistent and prove the reliability of this archive.

The pre-industrial CH₄ concentration changes, with some exceptions, in concert with the main climate features of the northern hemisphere. That is, lower concentrations of about 350 ppbv during ice ages, and higher concentrations, around 700 ppbv, during warm periods. Natural variations are most probably linked to the extent and source intensity of wetlands, the main natural source. The anthropogenic increase from 700 to over 1700 ppbv over the last 200 yr is caused by emissions linked to the human population growth like domestic ruminants, rice paddies, human-induced fires, landfills, and fossil fuel exploitation (FUNG *et al.*, J. Geophys. Res., 96, 13033, 1991 and references therein).

CH₄ can, due to its global signal (neglecting a pole to pole difference of a few percent), be used to synchronise ice core data from various sites. This is extremely useful in investigating the causes of climate change.

1. Introduction

In Fig. 1 the latitudinal concentration distribution in the period 1988 to 1997 is shown. The CH₄ rug shows three main characteristics: 1) a general concentration increase, 2) a latitudinal distribution with higher concentrations in the northern hemisphere, 3) annual variations of the CH₄ concentration which are anticyclic in the northern and the southern hemisphere with a maximum concentration in the respective winter season.

The concentration distribution is significantly affected by the distribution of sources and sinks. The major part (95%) of the CH₄ molecules released to the atmosphere are removed by reaction with the hydroxyl radical (OH). A small fraction of about 30 Tg (CH₄)/yr is removed in soils (HOUGHTON *et al.*, 1995). Over the year the OH distribution is symmetrical in latitude over the globe with maximal concentrations in the

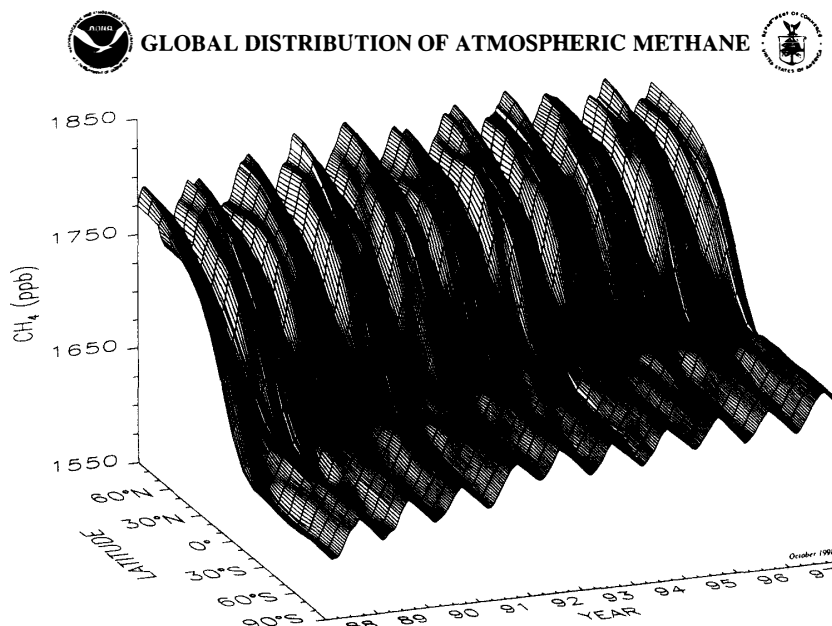


Fig. 1. Three dimensional representation of the latitudinal distribution of atmospheric methane in the marine boundary layer. Data from the NOAA CMDL cooperative air sampling network were used. The surface represents data smoothed in time and latitude. Principal investigator: Ed DLUGOKENCKY, NOAA CMDL Carbon Cycle Group, Boulder, Colorado, (303) 497-6228. edlugokencky@cmdl.noaa.gov.

Tropics. There are three principal processes leading to methane emissions: 1) production by bacteria under anaerobic conditions (wetlands, rice paddies, enteric fermentation, landfills), 2) emissions related to fossil fuel (coal, oil, natural gas), 3) incomplete burning of biomass. Source intensities have been estimated from today's CH_4 and $\delta^{13}\text{C}$ distribution (FUNG *et al.*, 1991; HEIN *et al.*, 1997). Present as well as past sources are landbound. Therefore maximum emissions occur in the northern hemisphere. Thus the imbalance between northern and southern CH_4 concentrations reflects the source distribution. The annual CH_4 variations are mainly caused by the annual cycle of the CH_4 sink, namely the OH radical, in the southern hemisphere and a combination of the annual cycle of sources, sinks and transport in the northern hemisphere (DLUGOKENCKY *et al.*, 1994).

The global mean concentration has increased about 1% per year (BLAKE and ROWLAND, 1988) with a slow-down during the most recent years (STEELE *et al.*, 1992; DLUGOKENCKY *et al.*, 1994). There is strong evidence that the increase is caused by the increasing agricultural and industrial activities of the growing human population.

2. Past CH_4 Concentration Recorded in the Ice of Glaciers and Ice Sheets

2.1. Recording of the atmospheric concentration

The paleo-archive of glaciers and ice sheets is unique as it is the only one which

records the atmospheric composition directly. Samples of atmospheric air are found in the bubbles of the ice. However, the archive samples not like a flask sample. The upper 50–150 m of an ice sheet are open porous; this section is called firn and it is but at the bottom of that zone where the gas is occluded in the ice. Therefore atmospheric air exchanges with the air in the firn. As a consequence the concentration of a gas species in the firn changes relative to its atmospheric concentration due to physical and in case of reactive gases chemical processes.

Although important for other gases, physi- and chemisorption of CH_4 at the surface of snow and ice is negligible and the concentration is not altered by such phenomenon (RASMUSSEN *et al.*, 1982; CHAIX *et al.*, 1996). The exchange process between firn air and the free atmosphere is dominated by molecular diffusion. Generally a quasi steady state is reached in the firn column where the downward flow due to gravitation is balanced by the diffusive upward flow due to the resulting concentration difference. This leads to a slight depletion of the CH_4 concentration with depth but only on the order of a few per mil. Therefore the measured concentration can generally be regarded as the atmospheric concentration. The occlusion leads as well to an age distribution in the firn. An air sample will not stem from one particular date but will be a mixture of air which was in contact with the atmosphere at different times. The standard deviation of the age distribution is site dependent and ranges from a few years for high accumulation sites to some centuries for low accumulation sites. See BLUNIER and SCHWANDER (1999) or SCHWANDER (1996) and references therein for additional information concerning the occlusion of gases and the importance of the processes involved.

Since the air is not occluded at the surface of the glacier the age of the gas in the air bubbles is less than the age of the surrounding ice. This age difference is temperature and accumulation dependent. The difference between the age of the ice and the age of the air under different climatic conditions can be assessed by determination of the depth of the firn-ice transition and the age of the ice at this depth using a firn densification model on one hand and calculating the age of the air at the transition depth with a diffusion model on the other hand (see SCHWANDER *et al.*, 1997 for details).

2.2. Analysis

Air trapped in the bubbles of the ice can be extracted in three ways: 1) crush the ice (ETHERIDGE *et al.*, 1992; FUCHS *et al.*, 1993; NAKAZAWA *et al.*, 1993a), 2) melt the ice (NAKAZAWA *et al.*, 1993a; CHAPPELLAZ *et al.*, 1997; SOWERS *et al.*, 1997), 3) sublimate the ice (GÜLLÜK *et al.*, 1998). In principle all methods are applicable for CH_4 analysis.

Gas initially enclosed in bubbles is forced to form clathrates (air-hydrates) under high pressure. Reformation of bubbles after core recovery is a slow process taking years to decades (UCHIDA *et al.*, 1994). While melting and sublimation extract the entire gas from bubbles and clathrates, crushing extracts mainly the gas from the bubbles. Since fractionation between the main air components and CH_4 takes place during formation and deformation of clathrates the CH_4 concentration from dry extractions may be altered below the clathrate formation zone. Such an effect has been observed within the clathrate formation zone of the GRIP ice core (BLUNIER *et al.*, 1995).

None of the extraction methods is free from contamination. For dry extractions the cause of the contamination is friction between metal surfaces. For the sublimation technique the contamination stems probably from desorption from the surface of the extraction chamber. The reason for contamination in the wet extraction technique is currently unknown. However, for each method the amount of the contamination can be determined accurately so that the corrected CH_4 values are reliable.

Generally, CH_4 is measured with a gas chromatograph equipped with a flame ionisation detector. Recently it has been demonstrated by GÜLLÜK *et al.* (1997, 1998) that absorption laser spectrometry can also be used for analysis of air from ice cores, with a reasonable amount of ice.

A recent comparison of standard gases and ice samples among four laboratories measuring CH_4 in ice cores has shown that all lead to comparable results within the experimental uncertainties, which is on the order of ± 20 ppbv (2σ) for most laboratories (SOWERS *et al.*, 1997).

Additional information concerning the contribution of different sources can be found in the isotopic ratios of carbon and hydrogen in CH_4 . $\delta^{13}\text{C}$ has been used as a constraint for the present day source distribution (FUNG *et al.*, 1991; HEIN *et al.*, 1997) and would also be useful to investigate the past distribution. However, such measurements on ice cores remain a challenge (CRAIG *et al.*, 1988). A recent study on firn air has shown that the $\delta^{13}\text{C}$ of CH_4 can be significantly biased by gravitational fractionation and diffusion (TRUDINGER *et al.*, 1997). δD of CH_4 has not been measured in ice cores so far and it is not clear whether the atmospheric signal is preserved in the bubbles of the ice.

3. Anthropogenic Increase

Ice cores from various sites have been investigated by several laboratories for the concentration changes of the previous centuries (CRAIG and CHOU, 1982; KHALIL and RASMUSSEN, 1982; RASMUSSEN and KHALIL, 1984; STAUFFER *et al.*, 1985; PEARMAN *et al.*, 1986; ETHERIDGE *et al.*, 1988, 1992; RAYNAUD *et al.*, 1988; BLUNIER *et al.*, 1993; DIBB *et al.*, 1993; NAKAZAWA *et al.*, 1993b; BLUNIER, 1996). All these measurements from sites with accumulation rates from a few centimetres to over 1 meter and various chemical impurities in the ice show an increase during the last 200 years from around 700 ppbv to about 1700 ppbv today.

This increase parallels remarkably well the human population increase (RASMUSSEN and KHALIL, 1984). The main reason for the concentration increase is the increase in the CH_4 sources associated with population growth such as domestic ruminants, rice paddies, human-induced fires, landfills, and fossil fuel exploitation (FUNG *et al.*, 1991 and references therein). A minor contribution of about 20% of the CH_4 increase results from the decrease of the CH_4 sink (OH radical) resulting from the increase of trace gases such as CH_4 and CO (THOMPSON, 1992).

Due to the enclosure process a time gap exists between the CH_4 signal recorded in the ice and the directly measured CH_4 concentration. This gap can be filled with data from firn air measurements. Using ice cores from high accumulation sites the time gap can be reduced and the time resolution of the CH_4 record can be increased.

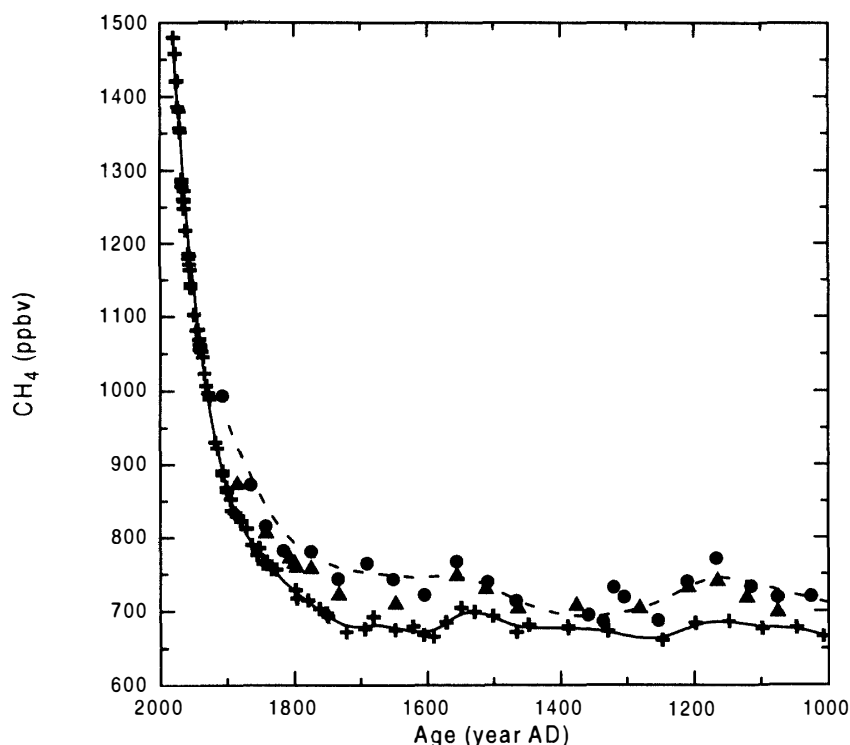


Fig. 2. CH_4 records covering the last millennium from ice cores: Crosses and filled triangles are from Law Dome Antarctica (firn measurements are not shown) and Summit Greenland, respectively from ETHERIDGE *et al.* (1998). Filled dots are results from the same Greenland ice core from the study by BLUNIER *et al.* (1993). Solid and dotted line are spline fits through the Antarctic and Greenland data sets, respectively. The difference between the Antarctic and Greenland records represents the distribution of CH_4 sources.

Recently the record from a high accumulation Antarctic site (ETHERIDGE *et al.*, 1992) has been detailed including also firn air measurements, and a remarkable fit to direct atmospheric measurements has been obtained (ETHERIDGE *et al.*, 1998). The results are shown in Fig. 2. The anthropogenic increase started around 1750 in accordance with data from Greenland with a lower time resolution (BLUNIER *et al.*, 1993). It was found that the growth rate has increased significantly and steadily since 1945, reaching its peak around 1981, and has been decreasing since. A reduction or stabilisation of fossil fuel emissions during this recent period is the most plausible explanation provided by ETHERIDGE *et al.* (1992), although other explanations cannot be ruled out (DLUGOKENCKY *et al.*, 1994; HEIN *et al.*, 1997).

The pre-industrial part of the last millennium has been analysed in detail from Greenland and Antarctic ice cores (BLUNIER *et al.*, 1993; NAKAZAWA *et al.*, 1993b; CHAPPELLAZ *et al.*, 1997; ETHERIDGE *et al.*, 1998). Variations are more distinct in the Greenland than in the Antarctic record and reach about 70 ppbv (Fig. 2). The interhemispheric difference varies between 24 ± 10 ppbv according to ETHERIDGE *et al.* (1998) in accordance with previous studies (NAKAZAWA *et al.*, 1993b; CHAPPELLAZ *et al.*, 1997).

The CH_4 variations parallel the main climatic features during this period. High CH_4 concentrations at the end of the 12th century correspond to the Medieval Warm Époque, and also the following Little Ice Age manifests by a decrease in the CH_4 concentration. Yet one must be careful comparing data to these events as they are globally inhomogeneous in space and in time. Variations of the oxidising capacity of the atmosphere can only explain the minor part of the pre-industrial fluctuation; the main contribution must stem from changes in methane emissions (BLUNIER *et al.*, 1993). Climatic fluctuations on this time scale have probably influenced the largest natural sources, *i.e.* the wetlands, but the lack of climate proxy data on a global scale precludes a quantitative estimate of this contribution. Finally, the role of the pre-industrial anthropogenic sources may have been significant but cannot account for the full amplitude of CH_4 variations. A human contribution is also supported by studies which show that the man made contribution to the CH_4 budget was significant before the major population growth (KAMMEN and MARINO, 1993; SUBAK, 1994).

4. Preanthropogenic Variations

4.1. Holocene

The Greenland ice cores provide a well dated CH_4 record over the Holocene (BLUNIER *et al.*, 1995). Generally, the Holocene is regarded as a time of constant climate; nevertheless, CH_4 shows significant variations of up to 15% over this period. The Holocene record was even more detailed (CHAPPELLAZ *et al.*, 1997) and reaches now a resolution of only 85 yr (Fig. 3). The highest concentrations are found during

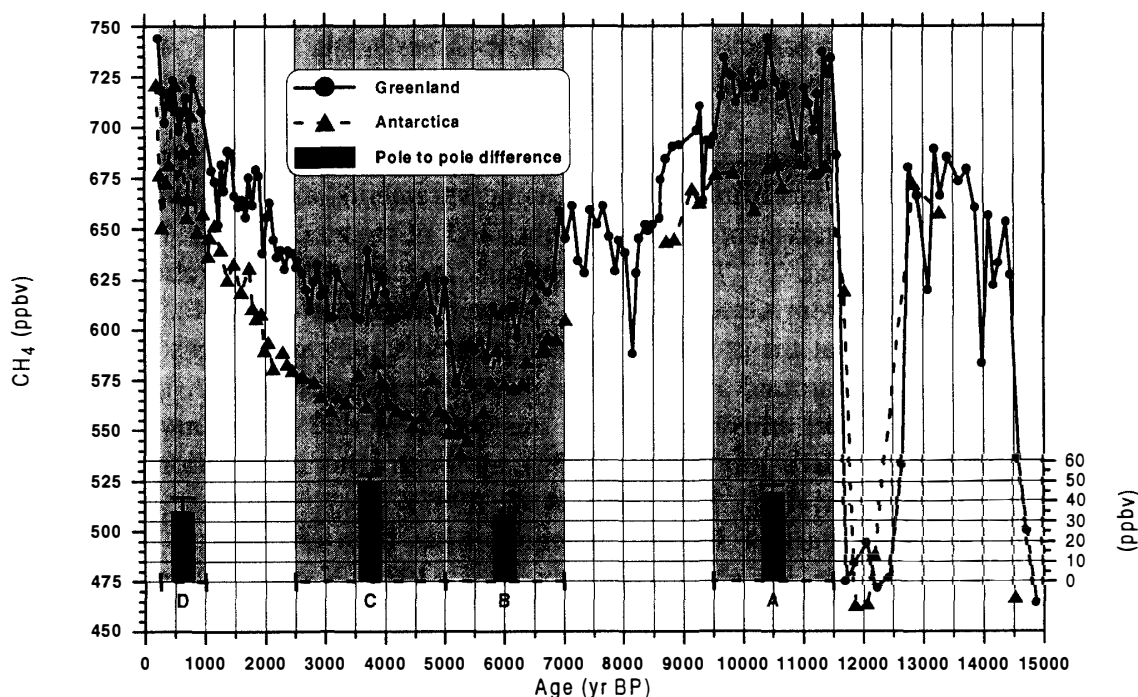


Fig. 3. CH_4 records covering the Holocene period in Greenland and Antarctic records with pole to pole differences over selected time periods from CHAPPELLAZ *et al.* (1997).

the first 2 kyr of the interglacial, and then not before the last millennium. During the mid-Holocene, concentrations are lower by as much as 100 ppbv. Thus the background CH_4 level over most of the Holocene stood rather around 650 ppbv than at the 700 ppbv interglacial level based on concentration measurements from the recent millennium. Superimposed on the general trend, which has no analogue in the GRIP isotopic record, are sharp drops of nearly 70 ppbv with a duration of 200 years at 10.9, 9.3 and 8.2 kyr BP. The last one is synchronous with a sharp drop in the Greenland $\delta^{18}\text{O}$ record and also with climatic events observed in other proxies (ALLEY *et al.*, 1997).

The Greenland record in combination with records from the Antarctic ice cores from D47 and Byrd have allowed to measure the inter-polar difference of the CH_4 concentration over the major part of the Holocene (CHAPPELLAZ *et al.*, 1997). This difference results from the latitudinal distribution of CH_4 sources and sinks. Significant changes of the inter-polar difference are observed around a mean value of 45 ± 3 ppbv (Fig. 3). This brings an additional constraint on the causes of natural CH_4 variability on the scale of an interglacial period, as discussed below.

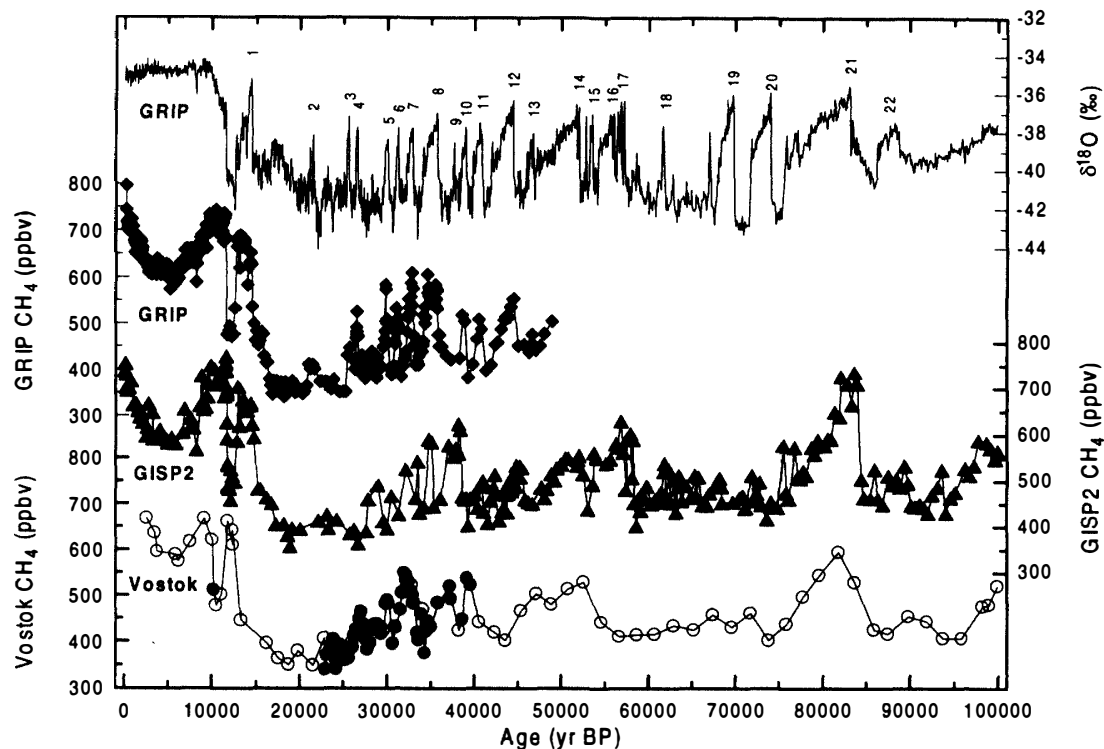


Fig. 4. Records reaching the last glacial from Vostok core in Antarctica and from the two Greenland drilling programs GRIP (CHAPPELLAZ *et al.*, 1997; BLUNIER *et al.*, 1998) and GISP2 (BROOK *et al.*, 1996). The initial Vostok record (CHAPPELLAZ *et al.*, 1990) was detailed in the time period 20–35 kyr for the synchronisation of climatic events by BLUNIER *et al.* (1998). It is remarkable that also very fast CH_4 variations are preserved in the low accumulation Vostok core. Note that each ice core is on its own individual time scale. Climatic events which are obviously identical may appear shifted. The $\delta^{18}\text{O}$ record from the GRIP core, a proxy for the Greenland temperature, is shown (DANSGAARD *et al.*, 1993). The well resolved CH_4 record changes in concert with this record.

4.2. Last Glacial

Initial measurements of the glacial CH₄ concentration showed that it nearly doubled from about 350ppbv to around 700ppbv from the Last Glacial (LG) to the Holocene (RAYNAUD *et al.*, 1988; STAUFFER *et al.*, 1988; CHAPPELLAZ *et al.*, 1990). Successively the CH₄ record was detailed and new results from the GRIP and the GISP2 cores confirmed the low 350ppbv level during the glacial but showed that CH₄ concentrations are able to change rapidly following the Greenland temperature signal (CHAPPELLAZ *et al.*, 1993a; BROOK *et al.*, 1996) (Fig. 4).

Greenland ice core isotopic records (DANSGAARD *et al.*, 1993; GROOTES *et al.*, 1993) have revealed 24 mild periods (interstadials) of 1–3 kyr duration during the LG (DANSGAARD *et al.*, 1993), known as Dansgaard-Oeschger (D-O) events (OESCHGER *et al.*, 1984), where temperature increased by up to 15°C compared to full glacial values (JOHNSEN *et al.*, 1995; SCHWANDER *et al.*, 1997). CH₄ concentrations change in concert with each of these events, except for D-O events Nr.19 and 20 (about 70 kyr BP) where no significant CH₄ variations were found. As during most D-O events the CH₄ concentration changes parallel to the Greenland temperature signal during the well-known cooling event of the Younger Dryas (YD) during the last deglaciation. The covariance of the CH₄ and the $\delta^{18}\text{O}$ signal shows a tight response of the natural CH₄ cycle to climate changes.

5. Climate Implications from CH₄ Records

Changes of the CH₄ concentration result from changes in source and sink intensities or their distribution. The main oxidant of CH₄ is the OH radical. Since OH is highly reactive, no direct measurements of the past OH concentration are available. The only possibility to reconstruct past OH concentrations is to look at constituents resulting from OH reactions. Such a species is formaldehyde. Unfortunately its transfer function from snow to ice is not well understood so far, preventing reliable conclusions for the past OH concentration (STAFFELBACH *et al.*, 1991; FUHRER *et al.*, 1993). The only means to investigate the past sink strength is through photochemical model studies (see for instance THOMPSON, 1992; CRUTZEN and BRÜHL, 1993; THOMPSON *et al.*, 1993; MARTINERIE *et al.*, 1995). All models suggest that OH concentrations were higher during glacial conditions than today, but not much larger than during the pre-industrial time. This means that a small part (10–30%) of the glacial-interglacial CH₄ increase can be attributed to decreased sink strength. The main reason for CH₄ concentration changes is definitely variations in the source strength. The largest source in pre-industrial times is natural wetlands, with a contribution of over 70% (HOUGHTON *et al.*, 1995). Other sources like termites, wild animals, wildfires, oceans and CH₄ hydrates in permafrost and continental shelves will have a weak impact on the concentration changes due to their small contribution.

CH₄ emissions from wetlands are generally correlated with soil temperature. However, it is believed that the main cause of potential changes in the CH₄ emission from wetlands is a change in global wetland area. The main part of the present-day wetlands lies between 50° and 70°N and in the Tropics, between 20°N and 30°S (FUNG *et al.*, 1991). The northern high latitude area of today's wetlands was covered by ice

sheets during the LG. Therefore a direct impact of the growth and decay of continental ice sheets at these latitudes on the CH₄ emissions has been suspected. CHAPPELLAZ *et al.* (1993b) used a parameterization of wetlands and other CH₄ sources on vegetation and topography distribution to quantify the CH₄ sources during the Last Glacial Maximum and the pre-industrial Holocene. They concluded that changes in the wetland CH₄ source were the major factor driving the CH₄ increase during the last deglaciation, with a dominant contribution from the northern mid and high latitudes.

However, in the glacial and also over the transition from the LG to the Holocene the main northern wetland regions were covered by ice sheets. Thus, past changes in monsoon intensity and the hydrological cycle at low latitudes could be responsible for the CH₄ variability observed from ice cores (CHAPPELLAZ *et al.*, 1993a). The concomitance between CH₄ changes and Greenland climate would indicate that these climatic features were not restricted to the North Atlantic region but involved a large part of the globe. Recently a link between climate changes seen in Greenland and monsoonal activity has been found (SCHULZ *et al.*, 1998). On the other hand BROOK *et al.* (1996) interpreted the lack of CH₄ increase during D-O events Nr. 19 and 20 as a result of a substantial increase in continental ice volume, reducing the CH₄ emissions from boreal wetlands and consequently favoured a boreal control on the CH₄ budget on short and long time scales.

Additional information on the CH₄ source distribution comes from quantification of the interpolar CH₄ difference. Using a three-box model of the atmosphere, CHAPPELLAZ *et al.* (1997) translated the measured differences observed during the Holocene into quantitative contributions of CH₄ sources in the Tropics and the middle to high latitudes of the northern hemisphere. The model assumed that the inter-box exchange time, the OH latitudinal distribution and the CH₄ source between 30° and 90° S remained similar to today. Source distributions among the model boxes are shown in Fig. 5. The model output suggests that the doubling of atmospheric CH₄ between the LG and the early Holocene originates from a 53 and 40 Tg/yr increase of the tropical and boreal sources, respectively. The tropical source most likely involved increased wetland extent accompanying the wettest episode of the Holocene in the Tropics (PETIT-MAIRE *et al.*, 1991; STREET-PERROTT, 1992). The most probable boreal source experienced favourable conditions for wetland development during the early Holocene. During periods 5–7 and 2.5–5 kyr BP on-going drying of the tropical regions (STREET-PERROTT, 1993), combined with massive peat growth in the boreal regions after 5 kyr BP, took place (GORHAM, 1991). The recent period 0.25–1 kyr BP reveals a small gradient combined with a return to high CH₄ levels. The model translates these observations into a major increase in the tropical source, which may come from local increase in wetness but also from a significant man made contribution to the CH₄ budget (KAMMEN and MARINO, 1993; SUBAK, 1994). According to the results from CHAPPELLAZ *et al.* (1997) the Tropics made a major contribution to the CH₄ budget over the last 20 kyr, modulated by significant changes in the mid-to-high northern latitude sources. Such an exercise remains to be performed over the last glacial period.

An alternative interpretation of the fast CH₄ increases during the LG and also over the transition from the LG to the Holocene is degassing of CH₄-hydrate reservoirs from permafrost regions and the continental shelves (NISBET, 1992). A sudden release of

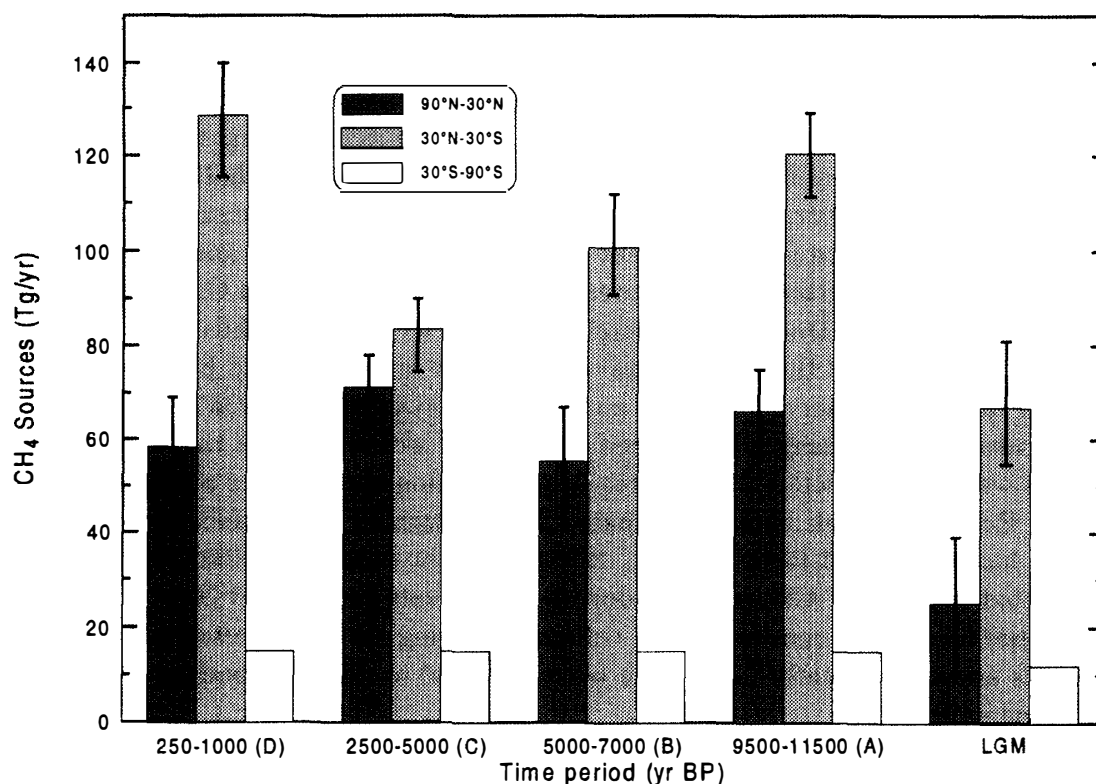


Fig. 5. CH_4 source distribution among three boxes of the atmosphere, for selected time intervals of the Holocene and for the Last Glacial Maximum, as deduced from changes in the interpolar CH_4 difference shown in Fig. 3 (CHAPPELLAZ *et al.*, 1997). Vertical bars are one-sigma confidence intervals.

vast quantities of methane hydrates from marine sediments or permafrost deposits (PAULL *et al.*, 1991; NISBET, 1992) would result in very high concentrations which would persist but a few decades due to the CH_4 lifetime of only ~ 10 yr (THORPE *et al.*, 1996). Growing evidence from the GRIP and GISP2 ice cores disproves such catastrophic scenario to have happened during the second part of the last deglaciation, in particular at the end of the YD and during the early Holocene (CHAPPELLAZ *et al.*, 1997; SEVERINGHAUS *et al.*, 1998). Further ice-core analyses over the first half of the deglaciation should provide a full test of the hydrate theory.

6. CH_4 as a Dating Tool

Fundamental to the understanding of processes involved in climate change is knowledge about their temporal and spatial evolution. Of special interest is the relation between high-latitude polar sites since they are a major component in climate change. Unfortunately, the dating of ice cores becomes more and more uncertain with increasing depth. For instance, the well dated GRIP core has an age uncertainty of ± 2 kyr at 40 kyr BP (JOHNSON *et al.*, 1992). For other ice cores where the glaciological flow regime is complicated by bedrock topography or melting at the bottom the dating may be even

less accurate.

In order to obtain at least good relative dating, ice cores have to be linked by markers. As long as the ice cores stem from the same hemisphere, many substances can be used, for instance volcanic ash layers or even the water isotopic record itself. However, few species are globally homogeneously distributed and therefore allow a link of ice cores from the two hemispheres. Such species are for instance $\delta^{18}\text{O}$ of O_2 and CH_4 , both have been used to synchronise ice cores. Variations in $\delta^{18}\text{O}$ (O_2) are rather slow and limit the accuracy of a synchronisation of the transition from the LG to the Holocene to about ± 600 yr (SOWERS and BENDER, 1995). CH_4 , with its fast variations in the glacial over the transition to the Holocene and also over the YD, is an excellent species to link ice cores. The slight concentration difference between the hemispheres is irrelevant when comparing the fast CH_4 changes. In theory the synchronisation of the gas records can be done with a accuracy of about 50yr (BLUNIER *et al.*, 1997). When comparing records stored in the ice the age difference between the ice and the gas has to be taken into account. In low accumulation areas this is the main uncertainty of the synchronisation.

Studies comparing ice core records based on CH_4 synchronisations have been done for the GRIP and GISP2 ice cores on the Greenland side and the cores from Byrd, Vostok and TAYLOR Dome on the Antarctic side (BLUNIER *et al.*, 1997, 1998; STAUFFER *et al.*, 1998; STEIG *et al.*, 1998) for the last 50 kyr. The main results are the covariance of CO_2 and the major D-O events and the asynchrony of Greenland and Antarctic temperature, Antarctic temperature leading by more than 1 kyr over the period 23–47 kyr BP. Results from Byrd and Vostok indicate that the Antarctic Cold Reversal took place before the YD, while at TAYLOR Dome no such event was found, but a kind of YD signal.

7. Summary

Atmospheric CH_4 measurements only exist since 1978. Before, CH_4 concentrations can be reconstructed reliably from air occluded in ice cores. The main features from these records are: (1) a large increase from 700 to 1700 ppbv during the last 200 years due to human activities; (2) a natural variability of up to 150 ppbv during the present interglacial, coupled with significant changes in the inter polar CH_4 difference, probably related to wetland dynamics in tropical and boreal regions; (3) rapid variations in the range of 350–700 ppbv during the last glacial. These CH_4 concentration changes generally occur in concert with the fast climate changes in the northern hemisphere. However, two exceptions to this general feature were found during D-O events 19 and 20 around 70 kyr BP. The main reason for the glacial CH_4 variations is probably fluctuations in low latitude wetland extent, although other reasons can not be completely ruled out.

A study for the Holocene period has shown that based on the interhemispheric gradient important information concerning the CH_4 sources can be obtained. Future work includes the inter polar CH_4 difference during glacial times and the CH_4 variability during previous climatic cycles. The isotopic composition of CH_4 ($^{13}\text{C}/^{12}\text{C}$ and D/H), if persistent in the ice archive, could be used to further identify past CH_4 sources.

Detailed CH₄ profiles make it possible to synchronise ice core records from both hemispheres. This allows for the first time, to discuss leads and lags of the climatic main events in the two hemispheres.

Acknowledgments

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